Faculty of Engineering

The Temperature Effects of Titanium Dioxide (TiO_2) Doped Reduced Graphene Oxide (rGO) for Perovskite Solar Cell Application

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. It is original and is the result of my work, unless otherwise indicated or acknowledged as referenced work. This thesis has not accepted for any degree and is not concurrently submitted in candidature for any other degree.

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ABSTRACT

Perovskite solar cells (PSC) are evolving in spectacular pace and emerging as the most promising future generation of photovoltaic devices. In the present study, reduced graphene oxide (rGO) is introduced to titanium dioxide (TiO_2) as electron transport layer (ETL) in perovskite solar cell (PSC). TiO_2 doped rGO (TiO_2/rGO) was prepared by combining titanium (IV) oxide nanopowder as precursor for TiO_2 and chemically reduced graphene oxide for rGO. The TiO_2/rGO is varied with different annealing temperature and its effect on TiO_2/rGO properties and on electrical performance of PSC is studied. The surface morphologies of TiO_2/rGO thin films is characterized via Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and X-Ray Diffraction (XRD). Meanwhile, Ultraviolet-visible spectroscopy (UV-Vis) and X-ray Photoelectron Spectroscopy (XPS) are used to characterize the optical properties and chemical bonding respectively. Lastly, (I-V) analysis for electrical properties is performed. Structural and morphological evidences from SEM, AFM and XRD results confirmed that the TiO_2/rGO samples existed in anatase phase, rutile phase and the porosity as well as the surface roughness of TiO_2/rGO thin films increased as the annealing temperature increased. The absorption spectra and the band gap obtained at 326 nm and 2.48 eV respectively for TiO_2/rGO that annealed at 550 ^{o}C portraits better performances due to increment in grain size in higher annealing temperature. The formations of Ti-O and Ti-O-C bonds are confirmed from XPS analysis that fastening the rate of electron transfer in PSC. The electrical properties of TiO_2/rGO confirming that 550 ^{o}C TiO_2/rGO has better conductivity at 18.83×10^{-3} S/cm in conjunctions with its performance in optical properties.

Keywords: Doping, perovskite solar cell, reduced graphene oxide, titanium dioxide.

Kesan Suhu Doping Titanium Dioksida (TiO_2) dengan Grafin Kurang Oksida (rGO) untuk Aplikasi Sel Solar Perovskite

ABSTRAK

Sel solar perovskite (PSC) telah berkembang dengan pesat dan muncul sebagai prospektif generasi masa depan untuk peranti fotovoltaik. Dalam kajian ini, grafin kurang oksida (rGO) dicampurkan dengan titanium dioksida (TiO_2) sebagai lapisan electron penghantar (ETL) dalam sel solar perovskite (PSC). Doping TiO_2 dengan rGO (TiO_2/rGO) telah dihasilkan melalui penggabungan titanium oksida (IV) dalam serbuk nano sebagai pendahulu untuk TiO_2 manakala rGO melalui pengurangan kimia daripada grafin oksida. TiO_2/rGO dihasilkan dengan suhu penyepuhlindapan yang berbeza dan kesannya terhadap sifat TiO_2/rGO dan prestasi elektrik dalam PSC dicatatkan. Mofologi permukaan filem tipis TiO_2/rGO dianalisa melalui Pengimbasan Elektron Mikroskop (SEM), Mikroskop Angkatan Atom (AFM) dan Difraksi X-Ray (XRD). Sementara itu, Spektroskopi Ultraviolet (UV-Vis) dan X-ray Photoelectron Spektroskopi (XPS) digunakan untuk mendapatkan sifat optik dan ikatan kimia. Akhirnya, analisis (I-V) untuk prestasi elektrik dilakukan. Struktur dan morfologi yang diperolehi daripada keputusan SEM, AFM dan XRD mengesahkan bahawa sampel TiO_2/rGO wujud dalam fasa anatase, fasa rutile dan keliangan serta kekasaran permukaan filem nipis TiO_2/rGO meningkat apabila suhu penyepuhlindapan meningkat. Spektrum penyerapan dan jurang band yang diperoleh pada 326 nm dan 2.48 eV menunjukkan bahawa TiO_2/rGO yang anil di 550 ^oC mempamerkan prestasi yang lebih baik disebabkan kenaikan dalam saiz butiran dalam suhu penyepuhlindapan yang lebih tinggi. Pembentukan ikatan Ti-O dan Ti-O-C disahkan dari analisis XPS mengawal kadar pemindahan elektron dalam PSC. Prestasi TiO_2/rGO dari segi elektrik mengesahkan *bahawa 550 ^{o}C TiO_2/rGO mempunyai kekonduksian yang lebih baik pada 18.83 × 10-3 S/cm bertepatan dengan prestasinya dalam sifat optikal.*

Kata kunci: *Doping, sel solar perovskite, grafin kurang oksida, titanium dioksida.*

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LIST OF ABBREVIATIONS AND SYMBOLS

Al_2O_2	Aluminium oxide
Au	Gold
C	Carbon
C-C	Carbon-carbon
C-O	Carbon-oxygen
COOH	Carboxylic
$CH_3NH_3PbBr_3$	Methylammonium lead bromide
$CH_3NH_3PbI_3$	Methylammonium lead iodide
DMF	Dimethylformamide
ETL	Electron transport layer
ETM	Electron transport material
FTO	Fluorine doped tin oxide
GO	Graphene oxide
HTL	Hole transport layer
HTM	Hole transport material
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
H_3PO_4	Phosphoric acid
$KMnO_4$	Potassium permanganate
Li-TFSI	Lithium bis(trifluoromethanesulfonyl)imide
O	Oxygen

OH	Hydrogen
PbI_2	Lead (II) iodide
PEG	Polyethylene glycol
PSC	Perovskite solar sell
rGO	Reduced graphene oxide
Spiro-OMeTAD	2’,7,7’-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene
TCO	Transparent conducting oxide
Ti	Titania
TiO_2	Titanium dioxide
TiO_2/rGO	Titanium dioxide doped reduced graphene oxide
TTIP	Titanium isopropoxide
ZnO	Zinc oxide
σ	Resistivity
ρ	Conductivity

CHAPTER 1

INTRODUCTION

1.1 Research Overview

Renewable energy tender opportunity of carbon-free economy for a greener and sustainable energy development in the world whereas the non-renewable energy sources produced enormous amount of carbon dioxide (CO_2) that harmful to environment and contribute to the hikes in climate changes and global warming (Nematollahi et al., 2016). Solar energy harvesting has been done substantially through photovoltaic devices as energy supply from the sun is reliable, renewable, and sustainable with no worry of depletion (Papoola et al., 2018). Thin film based photovoltaics solar cell such as copper-indium-gallium-selenide (CIGS), cadmium telluride (CdTe), dye-sensitized solar cell (DSSC), organic solar cell and perovskite solar cell (PSC) especially have caught research attention whereas by 2030 photovoltaic are anticipated as the third of global electricity generation (Green et al., 2014).

Perovskite solar cell has shown an increase in power conversion efficiency (PCE) at phenomenal rate in just seven years as compared to other type of photovoltaics. Perovskite is an organic-inorganic material that have shown its own capabilities for the use in light-emitting diodes, sensors, field-effect transistors and photodetectors (Assadi et al., 2018). Perovskite solar cells belong to the family of third generation of solar cell. The third generation of solar cell uses organic material in its fabrication that cut down the cost of making a solar cell. Perovskite solar cell also has display special combination of ambipolar charge transport properties, good broadband absorption and long carrier diffusion (Tonui et al., 2018).

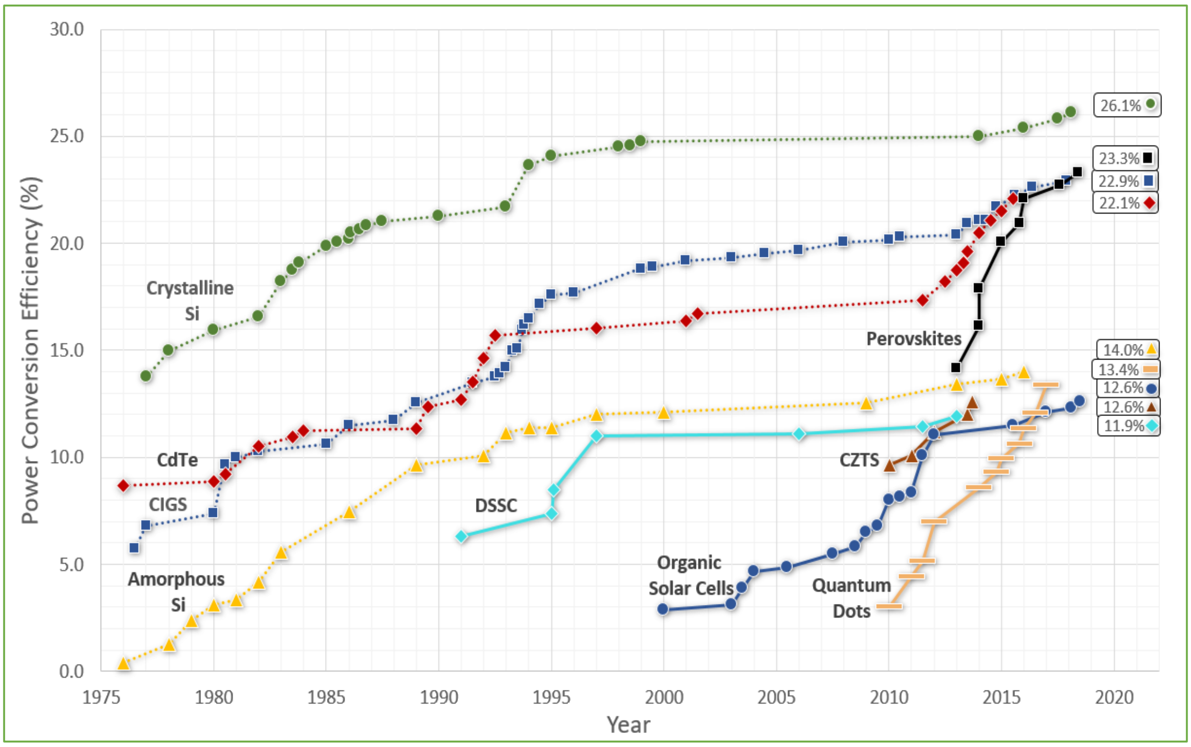

Figure 1.1: PCE for conventional photovoltaics (Best Research-Cell Efficiency Chart. (n.d.).

The first published perovskite solar cell was fabricated with methylammonium lead bromide ($CH_3NH_3PbBr_3$) as perovskite sensitizer and recorded 3.5% of power conversion efficiency (PCE) in 2009 (Tonui et al., 2018). Interestingly, the efficiency jumped to >15% after seven years later by making the perovskite material solid and cell design simpler with the use of methylammonium lead iodide ($CH_3NH_3PbI_3$) as perovskite material (Wu et al., 2014; Asghar et al., 2017). The high efficiency enabled the perovskite to compete with another conventional established technologies as shown in Figure 1.1. This dramatic increase in efficiency is due to the perovskite-based absorbers itself where it has larger capability to absorb photons than other conventional materials in making solar cells. In fact, it beats the industry-leading material silicon which it can absorb a larger spectrum of light (Mehmood et al., 2017).

Relatively, perovskite solar cells have two different configurations which are the meso-superstructured PSC and planar heterojunction PSC (Allesandro et al., 2016). In meso-superstructured device, the mesoporous layer typically made of metal oxide such as nano-crystalline titanium dioxide (TiO_2) and aluminium oxide (Al_2O_3) as scaffold infiltrated with perovskite solar cell. In this research, the nanocomposites reduced graphene oxide (rGO) and titanium dioxide (TiO_2) nanoparticles were utilized as electron transport layers in meso-superstructured perovskite solar cell. It has been reported that graphene-TiO_2 nanocomposites has the benefits of high conductivity and better electrical contacts of graphene and graphene-like materials for electron transporting. Furthermore, the highest PCE reported graphene-PSC works so far was done by Nicholas which had shown remarkable PCE up to 15.6% (Nicholas, 2013). This shows that the integration of graphene into PSC can compete with other intrinsic PSC in term of power conversion efficiency.

Further study on the graphene-PSC integration by using reduced graphene oxide (rGO) that synthesized through improved Hummer's method and chemical reduction is conducted in this research. The hole transporting layers (HTM) used in the PSC is highly expensive due to synthesis complexity. The material of choices here is 2,2',7,7'-tetrakis-(N, N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-oMETAD) which has been well studied due to its popularity in solid state dye solar cells (DSCs). In addition, its tendency to be uncontrollably doped by O^2 which necessitate the development of alternatives. An application of nanocarbons such as graphite, carbon nanotubes, and graphene/polymer composites based hole transporters is one of alternative worth to further investigated.

Next, the synthesis, characterization and the application of titanium dioxide doped reduced graphene oxide (TiO_2/rGO) as mesoporous layer in the fabrication of perovskite solar cell were studied and discussed. The performance TiO_2/rGO thin film and TiO_2/rGO-based perovskite is varied by the annealing temperature of titanium dioxide to enhance the electrical performances of perovskite solar cell.

1.2 Research Problem Statement

Resources for a clean and renewable energy is one of the challenges that our society have to face in order to allay with the rapidly increasing demand for the developing population and industrialization. The usage of non-renewable energy such as fossil fuels and others have contributed to rise of atmospheric temperature and high level emission of carbon dioxide (CO_2) that associated with the greenhouse effect (Khalaji et al., 2018). A lot of studies have been executed for solar energy harvesting that has been performed through photovoltaic devices. PSCs have been dominating research interest due to its impressive development in power conversion efficiency (PCE) that have reached 20% in over seven years of research as compared to other type of solar cell (Tonui et al., 2018). In spite of that, further improvement are imperative to optimize and enhance the PSC devices operation, stability and device performance. The aim is to construct photovoltaic device, an argonometal halide perovskite solar cell with $CH_3NH_3PbI_3$ as the absorber that coated upon the surface of mesoporous TiO_2/rGO.

Throughout the years, anatase TiO_2 was found to be the most common material to enhance photocatalytic properties of photoanodes in solar cell due to its long-term thermodynamic stability, low cost and relatively non-toxicity (Kang et al., 2019). However, the drawbacks are anatase TiO_2 tend to suffer from high recombination center of electrons and hole coupled with wide band gap which is 3.2 eV (Tan et al., 2013).

On the other hand, graphene has been widely used in application of optoelectronic and photon energy conversion due to its unique mechanical and electrical properties (Lundie et al., 2015; Chong et al., 2016). Some research was conducted and it is reported that rGO nanocomposites were an applicable additive for enhancing the charge collection properties in dye-sensitized solar cells (DSSCs), owing to its ability to reduce the charge-recombination pathways effectively and decrease the leakage current (Cho et al., 2016). More recently, Wang et al. reported that TiO_2/rGO composite based blocking layer is negatively effecting the energy barrier and series resistance between TiO_2 (Wang et al., 2014).

Therefore, it is believed that the induced of rGO in TiO_2 and its fabrication as TiO_2/rGO photoanodes in PSC utilizing the properties of graphene that have excellent electrical and optical properties merging with chemical stability in TiO_2 to increase PSC efficiency and to achieve good conductivity. Accordingly, the post annealing temperature dependence while synthesizing TiO_2-rGO solution and its performance as mesoporous layer in PSC is systematically studied in its surface morphologies, optical characteristic, chemical bonding analysis and current-voltage measurements.

1.3 Research Hypothesis

TiO_2 doped rGO that synthesized at different annealing temperature improve the performance of structural, optical, chemical bonding and electrical properties of TiO_2/rGO as fabricated in perovskite solar cell.

1.4 Research Gap

For research gap, there are two main finding of studies are discussed. First, it is studied from literature review that TiO_2 have three crystalline phase which are anatase, rutile and brookite. The phase changing often links to the annealing temperature used during synthesis. Previous work stated that TiO_2 will change its phase from anatase to rutile at annealing temperature of 700 ^oC and above (Fazli et al., 2016). Meanwhile the current study investigated annealing temperature from 450 ^oC to 650 ^oC with 100 ^oC increment that shown the presence of rutile phase in TiO_2 at 550 ^oC to 650 ^oC annealing temperature. This finding might surpassed the theory that only annealing temperature effecting the TiO_2 phase, might as well the surrounding atmosphere, the preparation methods or the type of chemicals used in preparing TiO_2 solution.

Secondly, in past few years, numerous perovskite fabrication has used mesoporous TiO_2 as electron transport material (ETM) with spiro-OMeTAD as HTM and $CH_3NH_3PbI_3$ as the absorber (Tonui et al., 2018). In the effort of finding the most reliable photovoltaic solar cells, research by research must be done to fully optimize the performances of solar cell. Then, the idea of doping the TiO_2 with rGO in conjunction with excellent properties of graphene has been introduced in DSSC as its photoanodes and has increased the efficiency of DSSC. In this wise, this research introduced the TiO_2 doped rGO in PSC configurations as its mesoporous layer with improvement in electrical properties of PSC.

1.5 Research Objectives

The aim of this research is to study the characterization of TiO_2 doped rGO (TiO_2/rGO) solution and its performance as thin mesoporous layer perovskite solar cell. In order to achieve the aim above, objectives of the research are as below:

(i) To examine the effects of 450 ^oC, 550 ^oC and 650 ^oC annealing temperature on TiO_2 doped rGO by structural, optical, chemical bonding analysis and electrical.

(ii) To fabricate $CH_3NH_3PbI_3$-based perovskite devices using spiro-OMeTAD as a hole transport layer and TiO_2 doped rGO as electron transport layer.

1.6 Scope of Research

This study focuses on modifying the electron transport layer in PSC. In this research, PSC is constructed with introduction of titanium dioxide doped reduced graphene oxide (TiO_2/rGO) layers as electron transport layer. The annealing temperature of titanium dioxide were varied at 450 ^oC, 550 ^oC and 650 ^oC. TiO_2 is prepared by using Titanium (IV) oxide nanopowder as precursor with addition of polyethylene glycol in its process. Meanwhile, for rGO solution, first the graphene oxide (GO) is prepared by using Improved Hummer's method, then the GO solution's obtained is chemically reduced to became rGO. Subsequently, the TiO_2 is doped with the rGO solution via nano-composite process to obtain the TiO_2/rGO mixture. Next, TiO_2/rGO is deposited by using spin coating technique for thin film characterization and fabricated as ETL to become perovskite solar cell.

Next, the performance analysis of TiO_2-rGO thin film and perovskite solar cell has been carried out focusing on its surface morphology, optical, chemical bonding structure and electrical properties. Various method are used to analyse this characteristic which are